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Electron-stimulated desorption of cations from dielectric matters: NaCl and H_2O nanoclusters adsorbed on a solid Ar substrate

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In order to gain insight into the behavior of charged particles in dielectric matters, electron-stimulated desorption of cations from NaCl and H_2O nanoclusters adsorbed on a solid Ar substrate has been investigated. It is found that hydrated protons, $H^+(H_2O)_n$, and Na^+ and $Na^+(NaCl)_n$ ions, respectively, are emitted from H_2O and NaCl nanoclusters, suggesting that most of the excess protons formed in water are hydrated, whereas bare Na^+ ions can exist in NaCl. The ion emission is induced by Coulombic repulsion of valence holes confined in the adsorbed nanoclusters. The ion yields decay almost exponentially with increasing coverage due to the delocalization of valence holes in the overlayer. No indication of the Coulombic ejection of Cl^+ ions based on two Cl $3p$ holes is obtained from NaCl nanoclusters. The Cl^+ ion is more likely to be emitted with a localized Cl $3s$ hole state.

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I. INTRODUCTION

The interaction between condensed molecules, or solvation of charged particles in matrices, is an important step of chemical reactions in a solvent. In electrochemistry, ion and electron transport through water is of fundamental interest, because water is the most important electrolyte. The underlying dynamical process in liquid water is believed to be making and breaking of hydrogen bonds, but ion-induced modifications of the hydrogen-bond properties in electrolyte are still elusive. A proton forms a weak chemical bond with a water molecule to give a hydronium ion, and the charge migration is characterized by successive jumps of a proton from one oxygen site to the next.[1] Recently, the solvation and transport of excess protons in water have been discussed extensively.[2–7] However, there exists considerable debate concerning its mechanism. More insight into the behavior of protons or other ions in solvent would be gained if they can be extracted from a surface into the vacuum.

Such a possibility might be explored in electron-stimulated desorption (ESD), since energetic electron impact produces charged particles in water. In the previous studies, however, very few ions except for protons are emitted from a monolayer as well as condensed multilayers of water formed on metal substrates.[8,9] Regarding the ion emission from highly ionic-compound surfaces, Knotek and Feibelman (KF)[10] proposed a simple model based on Coulombic repulsion in the ionic lattice as a result of the Auger decay of a core hole. This idea has been generalized to more covalent systems or even chemisorption systems on metals.[11–13] Coulombic repulsion is known to play an important role in dissociative ionization of gas-phase molecules,[14] as well as fission of suspended nanoclusters.[15] However, the occurrence of Coulomb explosion on condensed-matter surfaces is not well established in terms of the localization of multiple valence holes. For molecules adsorbed on metal substrates, possible ion desorption or dissociation channels might be quenched due to strong chemical interactions with the substrate. In this respect, weakly physisorbed substrates are of interest to investigate dynamical electronic properties of adsorbates themselves because electronic excitation would be confined in the overlayer for considerably long time without decaying into the substrate.

In this paper, the mechanisms of electron-stimulated positive-ion desorption are discussed for H_2O and NaCl molecules adsorbed on a solid Ar substrate, with emphasis on the nature of excess cations in matrix. The excess protons formed in water are emitted preferentially in the hydrated form rather than bare protons. From NaCl, bare Na^+ ions are emitted more intensively than the solvated ions, whereas Na^+ tends to be hydrated when a small amount of water coexists. The ion emission occurs as a consequence of Coulomb explosion between valence holes confined in adsorbed nanoclusters. The ion yield decays markedly with increasing coverage, since nascent valence holes are delocalized in thick H_2O and NaCl layers. On the basis of these experimental results, the KF mechanism for desorption of Cl^+ from NaCl is denied.

II. EXPERIMENT

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The electron beam was chopped by an electrostatic deflector into pulses with width 100 ns and frequency 40 kHz, so that the emitted ions were detected by the time-of-flight (TOF) technique. The TOF-ESD measurements were made in such a manner that a sample, floated with a bias voltage of $+500$ eV, was irradiated with a primary electron beam of 1 keV through the grounded stainless-steel mesh placed 4 mm above the sample surface (the electron impact energy was 1.5 keV), and the positive ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed electron beam with a low incident flux (0.5 nA/cm^2) was used. The substrate was a Pt foil mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by He^+ sputtering and annealing

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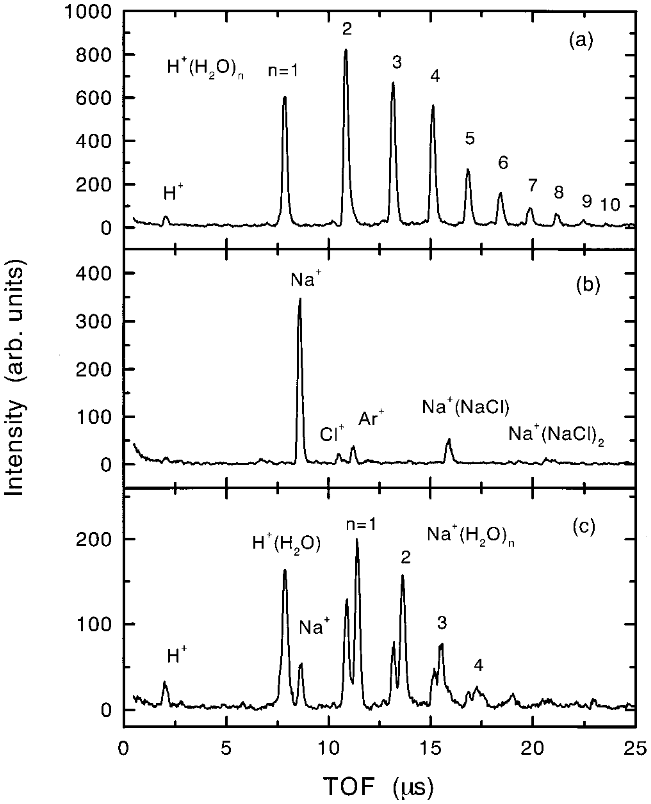

FIG. 1. TOF spectra of ESD ions from (a) H_2O, (b) NaCl, and (c) H_2O/NaCl adsorbed on the condensed Ar substrate (15 ML). The coverage of each adsorbate is around 0.1–0.2 ML.

around 1200 K in oxygen atmosphere. The one monolayer (1 ML) coverage of adsorbed Ar and H_2O was determined from the decay curve of the Pt surface-peak intensity in low-energy He^+ scattering (LEIS) as a function of exposure time. The film thickness was estimated on the basis of this value. NaCl was *in situ* deposited by thermal evaporation.

III. EXPERIMENTAL RESULTS

Figure 1 shows TOF-ESD spectra of positive ions emitted from (a) H_2O, (b) NaCl, and (c) H_2O/NaCl adsorbed on the solid Ar substrate (15 ML). The coverage of each molecule is about 0.1–0.2 ML. From the adsorbed H_2O molecule, hydrated protons of the type, $H^+(H_2O)_n$, $n=1,2,...,10$, are emitted intensively, together with the H^+ ion with a much smaller intensity. This result is remarkable in comparison with the previous ESD studies performed on metal substrates, in which H^+ is the dominant species.[8,9] Thus, the solid Ar substrate plays a decisive role in the emission of the $H^+(H_2O)_n$ ions. From the adsorbed NaCl, not only fragment ions Na^+ and Cl^+, but also cluster ions $Na^+(NaCl)_n$ are emitted. From the coadsorbate of H_2O and NaCl (coverage less than 0.2 ML), hydrated Na^+ ions, $Na^+(H_2O)_n$, desorb more intensively than bare Na^+ ions or hydrated protons.

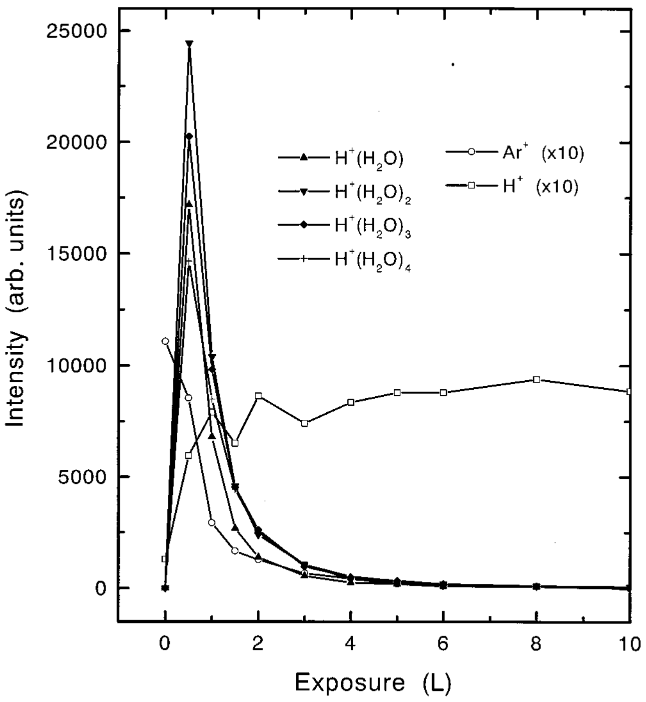

FIG. 2. Evolutions of typical ESD ion yields from H_2O adsorbed on the solid Ar substrate (15 ML) as a function of exposure.

In Fig. 2 we show evolutions of the ESD ions from the H_2O adsorbed Ar substrate as a function of exposure. The yield of Ar^+ from the substrate decays with exposure of H_2O due to the shadowing effect. From the decay curve, the Ar substrate is thought to be covered with the H_2O layer at an exposure of around 2–3 L ($1\ L = 1.0\times 10^{-6}$ Torr s), which is comparable to the exposure of H_2O to cover the Pt substrate as determined from the LEIS experiment. The yields of $H^+(H_2O)_n$ ions are the highest at small coverage and decay almost exponentially with increasing coverage; they become three to four orders of magnitude smaller than the maximum values at the thick H_2O layer (50 L). In contrast, the H^+ yield increases with exposure and tends to saturate above 5 L. The cluster ions are emitted even in the smallest coverage regime, indicating that the H_2O molecules agglomerate on the Ar substrate.

The evolution curves of the ESD ions from NaCl are shown in Fig. 3 as a function of the number of deposition of NaCl by the same amount. The measurements were made on three substrates; the Pt foil, solid water (30 ML), and solid Ar (15 ML). On the Pt and H_2O substrates, very few Na^+ ions are emitted from adsorbed NaCl at small coverages (less than three times deposition). In sputtering experiments, the complete neutralization of desorbing ions is known to occur if parent atoms and molecules are chemisorbed in the first monolayer.[16] Therefore, the multilayer of NaCl is thought to grow above four times of deposition. On the Ar substrate, the Na^+ and $Na^+(NaCl)_n$ yields are markedly enhanced below 1 ML coverage, but no enhancement of the Cl^+ yield occurs. With increasing coverage, the cluster ions disappear completely and the Na^+ yield becomes comparable to the Cl^+ yield. For the thick NaCl films, the results are essentially identical between Pt, solid H_2O, and solid Ar substrates. The Cl^+ ion is slightly detectable on the Pt substrate even in the chemisorption regime.

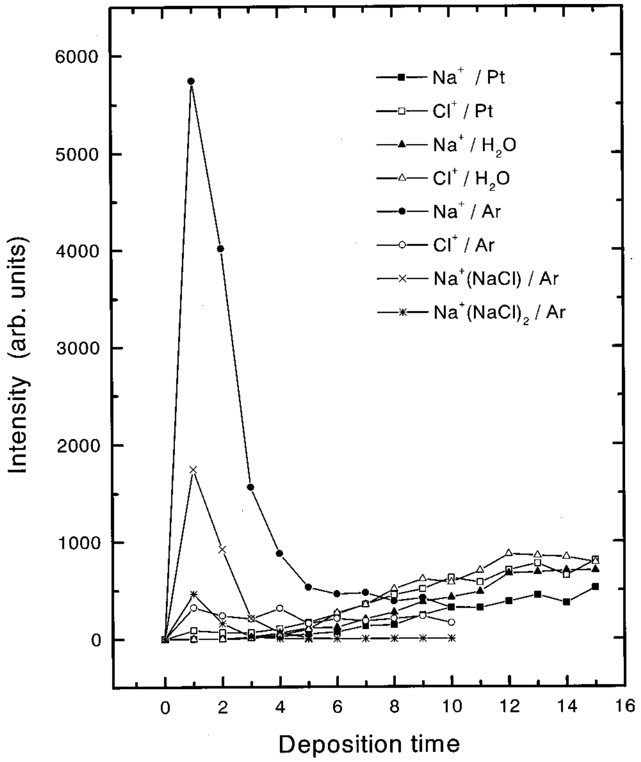

FIG. 3. Evolutions of ESD ion yields from NaCl adsorbed on the Pt, solid Ar (15 ML), and solid H_2O (30 ML) substrates. NaCl is deposited on the substrate several times by the same amount. The multilayer of NaCl starts to grow above four times deposition as inferred from the evolution of both Na^+ and Cl^+ yields that is characteristic of the ESD spectra of bulk NaCl.

IV. DISCUSSION

For both H_2O and NaCl adsorption on the solid Ar substrate, the ESD positive-ion yields are markedly enhanced at the smallest coverage. The emission of cluster ions indicates that adsorbed molecules form two-dimensional (2D) or 3D islands (clusters). The light ion species such as H^+ can be emitted due to dissociative ionization of individual H_2O molecules.[9] Therefore, it might be presumed that hydrated protons, $H^+(H_2O)_n$, are formed as a consequence of the incorporation of such H^+ ions at the surface or in the gas phase. In this respect, Prince and Floyd[17] reported that the $H^+(H_2O)_n$ ions are emitted from water ice at 153 and 193 K but no hydrated protons are observed at 77 K. At such high temperatures, H_2O sublimes in vacuum, so that the clustering about an energetic proton might occur in the gas phase. In the present experiment done at 15 K, however, such a possibility is discarded as evidenced by the completely different evolution curves between the H^+ and $H^+(H_2O)_n$ ions shown in Fig. 2. Coulomb explosion between valence holes or cations formed in a small cluster should be responsible for the emission of heavy ions, such as $H^+(H_2O)_n$, $Na^+(NaCl)_n$, and Na^+. The valence holes are formed due to the Auger decay of a core hole or the sequential two-electron excitation. In order for the Coulomb explosion to occur, the size of the clusters should be within the range of the Coulombic force ($<$1–2 nm). Another ingredient for the occurrence of Coulomb explosion is that the resulting valence holes should be localized in the adsorbed clusters for 10–100 fs corresponding to the ion desorption time. The ability of the confinement of valence holes is highly dependent on the substrate as shown in Fig. 3. Very few $H^+(H_2O)_n$ ions are emitted from water (0.1 ML) adsorbed on the thick NaCl layer as well.[18]

Regarding the formation of "nanoclusters" of H_2O and NaCl, no direct experimental evidence exists. Probably, the diffusion length of adsorbates at such a low temperature as 15 K is so short that a large number of nucleation sites for nanoclusters are created on the substrate. We can present a supporting evidence for this claim regarding the temperature dependence of the $H^+(H_2O)_n$ ions emission from the substrate of perfluorocarbon (Fluorinert, FC-77).[18] At small coverage of adsorbed water at 15 K, intensive $H^+(H_2O)_n$ yields comparable to those on the solid Ar substrate were obtained. However, the ion yields decay with increasing temperature and finally very few or no $H^+(H_2O)_n$ ions are emitted at 100 K despite that water exists on the surface. This behavior is ascribed to the surface diffusion of water molecules and the formation of larger-sized H_2O clusters.

Form the above context, comparison with the results of free nanoclusters would be instructive. The electronically excited clusters fission into smaller ones by the emission of neutrals and ions. Of interest is the fact that small multiply charged clusters are often unobservable in mass spectra as a consequence of Coulombic fission.[15] This occurs because the repulsive energy between positive holes exceeds the binding energy of molecules. The critical size has been determined for some clusters,[15,19–22] the doubly charged ions of Pb_n, $(NaI)_n$, Xe_n, Cs_n, Na_n, K_n, and Li_n clusters, respectively, are not observed in the mass spectra for n below 30, 20, 52, 19, 21, 27, and 25. It is also revealed that a magic number exists in size distributions of the daughter ions as a result of the shell effects on the stability of clusters.[21] In these studies, the doubly charged clusters are created in the mass spectrometer via the sequential one-electron excitation. However, Coulomb explosion is not necessarily quenched for parent clusters above such critical sizes. This is in fact the case for Coulomb explosion via the Auger decay of a deep core hole, which occurs if the resulting valence holes are localized in a nanometer-sized volume of larger clusters. The kinetic energy of daughter ions is expected be high for smaller-sized clusters.[21] The higher kinetic energy should be necessary for the ion desorption from adsorbed nanoclusters in order to overcome the image-charge attractive force.

A steep decay of the ion yield with increasing coverage of both NaCl and H_2O molecules is interpreted in terms of the delocalization of valence holes in the overlayer. It might be presumed that a valence hole tends to be localized in highly ionic compounds such as NaCl, as well as weakly condensed molecular solids such as H_2O. In this respect, the localization/delocalization of a valence hole on solid surfaces has been explored in low-energy (100 eV) H^+ scattering experiments,[23] where the H^+ ion experiences transient adsorption/desorption on a surface for around 5 fs. Therefore, the neutralization probability of H^+ is determined by the competition between the transient adsorption time and the lifetime of a valence hole on the surface. In the case of thick water ice, the H^+ ion (100 eV) scattered off oxygen atom forms transient $H^+(H_2O)_n$ species, but the scattered H^+ ion was neutralized considerably relative to that from solid O_2 and CO surfaces due to delocalization of a valence hole via the hydrogen bond.[24,25] On the other hand, the H^+ ions survive neutralization with a higher probability on the NaCl surface;[23] the surface peak intensity from Cl and Na is about an order of magnitude as large as that from O of H_2O. The H^+ ion is neutralized completely on the Pt substrate. Therefore, a valence (or H^+ $1s$) hole may be delocalized in order of Pt, H_2O, and NaCl. The delocalized nature of a hole in water ice has been ascribed to some covalency in hydrogen bonds.[24]

In the case of ESD, the duration of the ion-surface interaction is much longer than that in H^+ scattering because heavier ions with smaller kinetic energy (<5 eV) are relevant. It is apparent that two-holes localization (Coulomb explosion) is more difficult to take place than one-hole localization (survival of H^+ ions) because hole pairs undergo a strong repulsive force. Moreover, valence holes do not necessarily move along with atoms and molecules in solids because they can diffuse in the valence band much faster (1 fs) than the atomic motion (10–100 fs), especially in the presence of repulsive interactions. Probably, this is the reason for the absence of Coulomb explosion or the insufficient confinement of multiple valence holes in NaCl nanoclusters adsorbed on the solid water substrate, as well as H_2O nanoclusters on the thick NaCl substrate.

In contrast to the hydrated protons, the H^+ yield exhibits monotonic increase as shown in Fig. 2. This behavior is expected to occur if valence holes are localized in individual molecules, and the excited molecules formed in the deeper layer do not contribute to the ion emission. For the isolated H_2O molecule, the H^+ emission is shown to occur via the creation of two holes in the $1b_1$ and $3a_1$ orbitals or a hole in the $2a_1$ orbital (O $2s$ character) of H_2O.[9] The former is less likely because the relevant valence orbitals take part in the hydrogen bond with some covalency and, hence, valence holes should be delocalized. On the other hand, the latter is a localized semicore hole, so that the H^+ ion can be emitted from the dangling $(O^*H)^+$ bond via the dissociative ionization. The anomalously large yields of the $H^+(H_2O)_n$, $Na^+(NaCl)_n$, and Na^+ ions at the smallest coverage on the solid Ar substrate may be related to the enhancement of electron-excitation cross sections characteristic of Coulomb explosion; i.e., the electronic excitation not only of the topmost-layer molecules, but also of the interior molecules in a cluster takes part in the ion emission because valence holes, formed via the Auger decay of a core hole, are not localized in individual molecules but are shared in the cluster.

The role of excess proton and Na^+ should be similar in H_2O and NaCl clusters, but the evolution curves between H^+ and Na^+ are quite different as shown in Figs. 2 and 3. As already mentioned, this is because observed protons are emitted via the different mechanism. The absence of bare protons formed via Coulomb explosion indicates that they are solvated almost completely in solid water, whereas bare Na^+ ions should be the dominant cationic species formed in NaCl. The efficient solvation of such a Na^+ ion by coadsorbed water molecules is clearly seen in Fig. 1(c). The underlying mechanism for the cluster-ion formation is the ion-dipole interactions between H^+ (or Na^+) and H_2O, which may be reinforced by the hydrogen bond. Thus, the cluster ions formation should be related intimately to the nature of solvation of excess cations by matrix. In reality, however, two effects can modify the type of ionic species present in the system: (i) the fact that these molecules are formed in a system with two neighboring holes, which is not the usual situation for a hole in condensed H_2O and NaCl, can influence the structure of the resulting cluster ions and (ii) the Coulomb explosion itself can be associated with particular rearrangements of the particles and with fragmentation.

The KF mechanism has been presumed for the emission of both Na^+ and Cl^+ ions from thick NaCl layers.[26,27] A doubt has been cast on the validity of the KF mechanism since the ion emission can be quenched due to faster lattice relaxation.[28] Coulomb explosion does occur in the case of NaCl nanoclusters as seen in Fig. 3; the repulsion between excess Na^+ ions leads to anomalous enhancement of the Na^+ yield at small coverage, whereas the absence of such a behavior in the Cl^+ yield shows that two holes are hardly localized in the Cl ion. On a thick NaCl film, Coulombic repulsion would be suppressed considerably due to the delocalization of valence holes. Thus, the KF mechanism, assuming Coulombic repulsion between the preexisting Na^+ ion and the Cl^+ ion formed via the Auger decay of a deep core hole, should not occur in the ionic lattice of NaCl. The threshold energy for desorption of positive ions from NaCl is determined to be around 20 eV,[26] which corresponds well to the Cl $3s$ binding energy. Therefore, the ion emission can be initiated by the creation of such a semicore hole, which is followed by the ionization via the Auger decay during or after cleavage of the bond. The creation of a core hole may induce rearrangement of the valence (Cl $3p$) electrons to screen it, during which the antibonding state may be formed. The ionization of core-excited Cl* can take place in the gas phase after desorption is completed, so that the resulting Cl^+ ion can avoid the reneutralization even on the metal substrate (see Fig. 3).

The possibility of Coulomb explosion has been explored extensively using multiply charged ions[29–34] (MCI) because MCI induces highly charged domain on insulating surfaces due to sequential resonance and Auger neutralization. Apparently, the positive charges induced by MCI are much higher than those in ESD. The total secondary-ion yields from nonmetal surfaces, such as Si, alkali halides, organic layers, C_{60} etc., increase with the primary-ion charge state. The mass spectrometry analysis by Della-Negra *et al.*[31] revealed that the strongly increasing ion species with the charge state of the MCI is proton that comes from unknown hydrogen impurities (probably adsorbed water or hydroxyl group) on the CsI and Si (or SiO_2) surfaces, whereas the yields of heavier secondary ions (e.g., Cs^+ and Si^+) are not greatly influenced by the incident charge state. In the MCI bombardment of LiF, the F^+ yield also increases strongly with primary-ion charge.[32] Thus, proton and (light) halogen cations are the most frequently observed ion species in both ESD and MCI-induced potential sputtering. These ions are emitted even from the chemisorbed atoms and molecules, suggesting that they are caused by localized core-hole state. Thus, no experimental evidence has so far been presented for the occurrence of the Coulomb explosion of cations even from highly insulating dielectric surfaces. This is because valence holes are delocalized in ordinary bulk materials due to the band effect.

V. SUMMARY

The mechanism of the electron-stimulated cations desorption has been investigated from adsorbed H_2O and NaCl molecules, with emphasis placed on the localization or delocalization of valence holes. The weakly physisorbed Ar substrate is effective in the confinement of valence holes in the overlayer, thereby enabling us to gain insight into the properties of adsorbed molecules or clusters themselves. It is found that hydrated protons, $H^+(H_2O)_n$, and Na^+ and $Na^+(NaCl)_n$ ions, respectively, are emitted from adsorbed H_2O and NaCl. The ion yields are highly enhanced at the smallest coverage and decrease markedly with increasing coverage. This behavior is explicable in terms of the Coulomb explosion of doubly charged nanoclusters and the delocalization of valence holes in thick overlayers. The preferential emission of protonated water-cluster ions indicates that most of excess protons tend to be hydrated in water due to the strong ion-dipole interactions, whereas the dominance of the Na^+ yield from NaCl suggests that bare Na^+ ions exist in solid NaCl. No evidence for the Coulombic ejection of Cl^+ ions from NaCl nanoclusters is obtained, because two valence holes are hardly localized in the Cl^- ion. The Cl^+ and Na^+ ion emission from a thick NaCl layer is more likely to be initiated by the Cl $3s$ hole state, which is followed by the ionization via the Auger decay during or after desorption.

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